therefore easy to estimate with reasonable accuracy. In the case of the lighter elements considered, the errors in the computation of the transmission factors may be as large as ±25%. Statistical counting errors and systematic errors introduced in the background subtraction procedure constitute another 5%. The cumulative standard errors quoted in Table III were computed in the usual manner assuming that the errors from each of the sources listed are statistically independent. They range from about ±20% in the heavy elements to ±30% in the lighter ones. The error quoted for the silver measurement is smaller because many measurements were made in this case with differing thicknesses. In addition, the results obtained using the Cd^{109} source were included in calculating the final ω_{KL} value for silver. In spite of the large experimental uncertainties, the comparison with previous measurements is meaningful since many of the other measurements differ from the present results (and from each other) by more than the quoted errors. In any event, it is safe to say that some of the error estimates on previous measurements may have been optimistic. Furthermore, there is also little question that more accurate measurements of fluorescence yields would be desirable.

The behavior of ω_{KL} as a function of Z is in good accord with theoretical expectations.[9] The magnitude of ω_{KL} should decrease slowly as a function of Z. In this region of the periodic table the change in ω_{KL} as a function of Z is considerably smaller than in the region considered in Ref. 1. This is not surprising, because the change in quantum energy of the L x rays as a function of Z is smaller in this region than for higher values of Z.

ACKNOWLEDGMENTS

The authors are grateful to Arnold Kirkewoog and Edward Zaharis for helping to construct some of the equipment used in these experiments.

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[9] M. A. Listengarten, Izv. Akad. Nauk SSSR Ser. Fiz. **24**, 1041 (1960); **25**, 792 (1962); **26**, 182 (1962).

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Double Excitation of Helium by Electron Impact

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This study is devoted to the theory and calculation of cross sections for the electron-impact excitation of doubly-excited states in helium which are stable to autoionization. The cross sections are found to exhibit sharp peaks just above the threshold energies for excitation and to decrease rapidly with further increase of energy. The maximum value of the Born-Oppenheimer cross section for excitation of the $(2p)^2\,{}^3P_g$ state is about 6×10^{-4} $(a_o)^2$ and occurs at approximately 11 eV above threshold. The cross sections for excitation of the $2p3p\,{}^1P_g$, $2p3d\,{}^3D_u$, and $2p3d\,{}^1D_u$ states are all less than 35 b. The cross section for the $(2p)^2\,{}^3P_g$ state has been calculated according to the Born-Oppenheimer, distorted-wave, and two-state strong-coupling approximations. In all of these cases the maximum amplitude of the scattered beam occurs at right angles to the direction of the incident electrons. The cross sections of the potential-and-exchange-distortion method (DEW) and of the complete two-state strong-coupling approximation are virtually identical. The Born-Oppenheimer approximation produces remarkably similar results. Rigorous upper bounds to the energies of the $2p3p\,{}^1P_g$, $2p3d\,{}^3D_u$, and $2p3d\,{}^1D_u$states of helium are reported. Finally, the cross sections are calculated in Born-Oppenheimer approximation for electron-impact excitation of the $(1s)^2(2p)^2\,{}^3P_g$ and $(1s)^2 2p3p\,{}^3P_g$ states of beryllium. The peak values of these cross sections are 12 $(a_o)^2$ and 2$(a_o)^2$, respectively.

I. INTRODUCTION

Although there is considerable evidence of discrete atomic states with energies which lie within the continuum for single ionization, until very recently little attention had been directed to the properties of these states. Indeed, their very existence often comes as a surprise to those who have been schooled in the doctrine that beyond the ionization potential all is chaos. The persistence of such highly energetic states for periods of as much as a microsecond invariably can be traced to the selection rules for autoionization, that is, the selection rules for the internal conversion process whereby an electron is shed from the atom. Our own interest in these states has grown from an initial conjecture that they may be involved in the formation of the diatomic ions HeA^+ and $NeXe^+$. Thus, Munson *et al.*[1] have reported appearance potentials for these ions which lie above the lowest ionization potential of A and Xe, but below the lowest excited states of He and Ne, respectively. While it is certainly possible that the helium and neon negative

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[1] M. S. B. Munson, J. L. Franklin, and F. H. Field, J. Phys. Chem. **67**, 1 (1963).

ionic states found recently by Schulz[2] and Simpson and Fano[3] could be responsible for these reactions, discrete states imbedded within the continua of A^+ and Xe^+ still remain likely candidates. These states can be produced experimentally by an impacting electron which either succeeds in exciting two atomic electrons simultaneously or in bringing forth a single atomic electron from an inner shell. It is our purpose here to investigate the electron impact cross section for the former of these two processes.

In helium all the doubly-excited states lie above the lowest ionization potential of the atom. If one of these is strongly coupled with neighboring levels in the continuum, the quasidiscrete state then will exhibit instability in the sense that one of the electrons can be spontaneously ejected from the atom. This internal conversion process is called autoionization. Selection rules follow immediately from the formula for the probability of autoionization, which in first-order perturbation theory is given by $P=(2\pi/\hbar)|V|^2$, where $V=\int\int d\mathbf{r}_1 d\mathbf{r}_2 \psi_i^*(e^2/r_{12})\psi_f$. Here ψ_i denotes the wave function for the quasidiscrete state, and ψ_f a continuum state of the same energy. If V is not to vanish, the two states must have the same parity and J values, and in the case of L-S coupling they must have the same L and S values. When these selection rules are applied to helium it is found that among the states which autoionize are those with the term symbols S_g, P_u, D_g, F_u, e.g., all states with s orbitals.

Doubly-excited atoms[4] and/or molecules are intrinsically interesting because of their highly energetic states. They undoubtedly share or even exceed the enormous reactivity of the singly-excited species. Consequently their importance as initiators of reactions involved in radiation chemistry and in the chemistry of high-temperature gases should be considerable.

Despite the fact that states of this sort are common to many atomic and molecular species, our attention here will be devoted almost exclusively to those states of helium which are stable to autoionization. Thus, we wish to avoid in this initial investigation the complexities of the many-electron atom and to gain experience concerning the dependence of the calculated cross sections upon the choice of scattering theory. With this in mind three scattering calculations have been performed. In the order of their increasing complexity and presumed accuracy these are the approximations of Born-Oppenheimer, of the distorted-wave method, and of the two-state method with strong coupling.

To calculate cross sections for electronic impact excitation of helium from the ground state, $(1s)^2\,{}^1S_g$, to one of its doubly-excited configurations, we shall make use of the nonrelativistic Schrödinger equation and neglect the effects of spin-orbit coupling. Furthermore, the system wave function will be approximated by a linear combination of terms involving the initial and final states of the target atom. The coefficients in this expansion are to be identified as the wave functions for the scattering electron. We then invoke the Hulthén variational principle and Hartree-Fock trial functions[5] in order to generate a set of approximate "moment" equations for the radial component wave functions of the scattering electron. By solving these equations subject to suitable boundary conditions one then obtains the phase shifts and cross sections of this two-state Hartree-Fock approximation. Because of the truncated nature of the two-state wave function it is imperative that the trial function be explicitly antisymmetrized in the three electrons.[6] In this theory no allowance is made for the effects of polarization, i.e., for those contributions to the system wave function which are commonly estimated by the method of perturbed stationary states.[7]

Calculations based upon this "complete two-state" theory are probably about the best that can be done at the present time. However, other estimates of the cross sections are obtained by introducing the additional approximations which lead to the simpler distorted wave and Born theories. Since we intend to perform calculations of cross sections for atomic and molecular species other than helium, it is highly desirable to determine whether these less involved and less expensive techniques lead to reliable results. In what follows we first consider the relatively uncomplicated Born approximation, and then proceed to a systematic development of the two-state theory from which the distorted-wave approximation develops as a special case.

As a further simplification, quite apart from the approximations involved in the scattering theory, it will be assumed that the wave functions of the target helium atom can be represented adequately by products of hydrogenic orbitals.

II. BORN-OPPENHEIMER APPROXIMATION

In this approximation it is assumed that the initial plane-wave character of the wave function for the incident electron is preserved throughout the collision process. Since detailed descriptions[8] abound in the

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[2] G. J. Schulz, Phys. Rev. Letters **10**, 104 (1963).

[3] J. A. Simpson and U. Fano, Phys. Rev. Letters **11**, 158 (1963).

[4] During the past year and a half, a strong interest in the properties of doubly-excited states has been revived. A critical survey of the literature from 1928 to December 1963, appears in the thesis of one of the authors [P. M. Becker, University of Minnesota, March, 1964 (unpublished)]. Another summary was presented recently by E. Holøien, Phys. Norvegica **1**, 56 (1961).

[5] T.-Y. Wu and T. Ohmura, *Quantum Theory of Scattering* (Prentice-Hall Inc., Englewood Cliffs, New Jersey, 1962), Chap. 1, p. 57, and Chap 3, p. 197.

[6] M. J. Seaton, in *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962), Chap. 11, p. 374.

[7] P. G. Burke and H. M. Schey, Phys. Rev. **126**, 163 (1962); A. Temkin and E. Sullivan, *ibid.* **129**, 1250 (1963).

[8] With the inclusion of exchange the Born approximation is commonly referred to as the Born-Oppenheimer approximation (BO). This is not to be confused with the Born-Oppenheimer separation of electronic and nuclear motions.

literature, we shall dwell here only on the novelties which are specific to the calculations of cross sections for doubly-excited states.

In the Born-Oppenheimer (BO) approximation the differential cross sections for exciting singlet and triplet states of helium are given by[9,10]

$$I(\theta,\phi)=(k/k_0)\textstyle\sum_m|f_{dm}(\theta,\phi)-f_m(\theta,\phi)|^2, \qquad (1)$$

and

$$I(\theta,\phi)=(k/k_0)\textstyle\sum_m|\sqrt{3}f_m(\theta,\phi)|^2,$$

respectively. Here

$$f_{dm}=\left(\frac{1}{4\pi}\right)\int\int\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 e^{-i\mathbf{k}\cdot\mathbf{r}_3}\psi_m{}^*(12)(4/r_3-2/r_{13}$$
$$-2/r_{23})e^{i\mathbf{k}_0\cdot\mathbf{r}_3}\psi_0(12), \qquad (2)$$

and

$$f_m=\left(\frac{1}{4\pi}\right)\int\int\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 e^{-i\mathbf{k}\cdot\mathbf{r}_3}$$
$$\times\psi_m{}^*(12)(H-E)e^{i\mathbf{k}_0\cdot\mathbf{r}_1}\psi_0(23),$$

are the direct and exchange contributions to the scattering amplitude, and the subscripts m refer to the various components of a degenerate atomic state. In atomic units the Hamiltonian is given by

$$H=,-.\nabla_1{}^2-\nabla_2{}^2-\nabla_3{}^2-4/r_1-4/r_2$$
$$-4/r_3+2/r_{12}+2/r_{13}+2/r_{23},$$

and the total energy by $E=\epsilon_0+k_0{}^2=\epsilon_m+k^2$, where ϵ_0 and ϵ_m refer to the atomic energy eigenvalues for the ground and excited states. Here $\mathbf{k}_0$ and $\mathbf{k}$ are the propagation vectors for the incident and the ejected electrons. As a matter of consistency we shall use for ϵ_0 and ϵ_m values calculated from our approximate atomic wave functions rather than the more accurate values which are available. In Appendix A we discuss the explicit forms for the wave functions and the energies calculated from them.

The lowest five states which are not subject to autoionization are $(2p)^2\,{}^3P_g$, $2p3p\,{}^1P_g$ and ${}^3P_g$, and $2p3d\,{}^1D_u$ and ${}^3D_u$. Of these one anticipates that the first will have the largest cross section, since it is the lowest of the doubly-excited states which is stable to autoionization. We do not calculate the cross section for the $2p3p\,{}^3P_g$ state because of the considerable algebraic complexity engendered by the requirement that its wave function be made orthogonal to that of the $(2p)^2\,{}^3P_g$ state. Excitation of the ${}^1D_u$ state is optically allowed by the two-electron selection rules of Goudsmit and Gropper.[11] It is therefore of interest to compare the magnitude of the electron impact cross section for this state with those for the forbidden transitions to P_g states.

The differential cross sections for the four excitations we have considered are given by

$$I(\theta,\phi;{}^3P_g)=(6k/k_0)|f_1(\theta,\phi;{}^3P_g)|^2,$$
$$I(\theta,\phi;{}^1P_g)=(2k/k_0)|f_1(\theta,\phi;{}^1P_g)|^2,$$
$$I(\theta,\phi;{}^3D_u)=(6k/k_0)(|f_1(\theta,\phi;{}^3D_u)|^2+|f_2(\theta,\phi)|^2), \qquad (3)$$
$$I(\theta,\phi;{}^1D_u)=(2k/k_0)(|f_1(\theta,\phi;{}^1D_u)|^2+|f_2(\theta,\phi)|^2),$$

where

$$f_1(\theta,\phi;{}^3P_g)=-(N/6)(\alpha^3\beta^3)^{1/2}\gamma^5 J_1J_2\sin\theta e^{-i\phi},$$
$$f_1(\theta,\phi;{}^1P_g)=-(2N/243)(2\alpha^3\beta^3\gamma^5\delta^5)^{1/2}$$
$$\times(J_1J_4-J_3J_2)\sin\theta e^{-i\phi},$$
$$f_1(\theta,\phi;{}^3D_u)=(4N/243)(\alpha^3\beta^3\gamma^5\delta^7/6)^{1/2}$$
$$\times(0.6J_1J_6\cos\theta-J_5J_2)i\sin\theta e^{-2i\phi}, \qquad (4)$$
$$f_1(\theta,\phi;{}^1D_u)=(4N/243)(\alpha^3\beta^3\gamma^5\delta^7/6)^{1/2}$$
$$\times(0.6J_1J_6\cos\theta+J_5J_2)i\sin\theta e^{-2i\phi},$$
$$f_2(\theta,\phi)=(4N/243)(\alpha^3\beta^3\gamma^5\delta^7/6)$$
$$\times(0.6J_1J_6\sin\theta)i\sin\theta e^{-2i\phi}.$$

Formulas for the functions J_i are presented in Appendix B. The values chosen for the screening constants α, β, γ, and δ and the defining formula for the normalization factor N are given in Appendix A.

The configurations of the doubly-excited states which are stable to autoionization do not contain s orbitals and so the direct scattering amplitude f_{dm} given by (2) is zero. Of all the terms in the operator $(H-E)$ only $(-2/r_{23})$ provides a nonzero contribution to f_m. There is no contribution to the scattering amplitude from the degenerate component of the atomic state with $m=0$. Equal contributions to the cross section arise from components with m values which are equal in magnitude but opposite in sign.

The differential cross sections for the P states vary with the direction of the scattered electron as $\sin^2\theta$. The cross sections for the D states vary nearly in the same fashion, having $\sin^2\theta$ as a factor. In Fig. 1 the differential cross sections for the D states are plotted for several energy values. The values for the total cross section $\sigma=\int d\phi\int d\theta\,\sin\theta I(\theta,\phi)$, which were obtained by a simple analytical integration, are presented in Fig. 2. It will be noted that curves (a) and (b) in Fig. 2 refer to Born cross sections calculated with two different choices for the ground-state wave function. For curve (a) we have used a two-screening-constant approximation with different orbitals for different spins; curve (b) refers to a ground-state function constructed of two orbitals with common screening constants. A more detailed discussion of these atomic wave functions is given in Appendix A. A comparison of these results clearly illustrates that the calculated cross sections are quite independent of which of these two functions one uses.

The cross sections for the states other than $(2p)^2\,{}^3P_g$ are so small that their peak values may be measured

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[9] H. Massey and B. L. Moiseiwitsch, Proc. Roy. Soc. (London) **A258**, 147 (1960).

[10] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), 2nd ed., Chap. 9, p. 244.

[11] S. Goudsmit and L. Gropper, Phys. Rev. 38, 225 (1931).

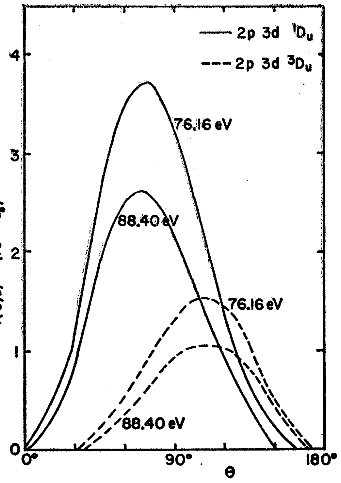

FIG. 1. Differential cross sections in Born-Oppenheimer approximation for the $2p3d\,^1D_u$ and $2p3d\,^3D_u$ states of helium at two different energies. The cross sections are plotted as functions of the scattering angle.

conveniently in barns. The past experience of other investigators has been that for impacting energies near threshold the cross sections predicted by the BO theory are invariably much too large. Therefore we assume that the BO calculations provide upper limits for these unlikely processes and consider them no further.

The $\sin^2\theta$ dependence of the differential cross section is so remarkable that it seems worthwhile to repeat here the qualitative explanation of this phenomenon which we reported earlier.[12] One can strongly contend that the incident electron must be captured into the p orbital which is oriented parallel to the initial direction of approach $\mathbf{k}_0$. Therefore, in the final $(2p)^2\,{}^3P_g$ state, the other bound electron must lie in one of the p orbitals oriented perpendicular to $\mathbf{k}_0$. From the preferential direction of ejection of the third electron it then can be argued that the intermediate complex, a helium negative ion, is composed of a singly-occupied p orbital oriented along $\mathbf{k}_0$ and a doubly-occupied p orbital perpendicular to this direction.

This unusual angular dependence is also predicted by the two-state theory presented in the following section. Consistent with this is the proof by Fano[13] that there is no forward scattering for an atomic state with even parity and odd L.

III. TWO-STATE THEORY

In general, one can expand the wave function for the composite system of scattering electron and target atom in a complete set of atomic eigenfunctions. The basic premise of the two-state theory is that an accurate estimate of this wave function can be obtained by limiting the expansion to terms which involve only the initial and final states of the atom. Because this truncated expansion does not include summation over the continuum states of the target, the approximate wave function must be antisymmetrized explicitly in order that it exhibit the correct asymptotic behavior.[6]

The most significant effect of our neglect of spin-orbit coupling is that the total spin and orbital angular momenta of the three-electron system will be separate constants of the motion. Since we are interested exclusively in the impact excitation of helium from the singlet ground state, the total spin always will be equal to $\frac{1}{2}$. The spin eigenfunctions for this doublet state, denoted by $\chi^+(12,3)$ and $\chi^-(12,3)$,[14,15] are, respectively, symmetric and antisymmetric to interchange of the spin coordinates of electrons Nos. 1 and 2. Therefore, these two functions are appropriate for the description of composite states involving triplet and singlet states of the atom.

According to the general quantum-mechanical rules for the addition of angular momenta the two-state wave function in the LSMM$_s$ representation may be written as[16]

$$\begin{aligned}\Phi(123)=\sum_{\text{cyc}}\Big\{&\sum_{l_2'}\sum_{m_1'}\sum_{m_2'}C(l_1',l_2',L;m_1',m_2',M)\psi_0(12)\\&\times r_3^{-1}F_0(r_3,l_2')Y_{l_2'm_2'}(3)\chi^-(12,3)+\sum_{l_2}\sum_{m_1}\sum_{m_2}\\&\times C(l_1,l_2,L;m_1,m_2,M)\psi_{m_1}(12)r_3^{-1}F_t(r_3,l_2)\\&\times Y_{l_2m_2}(3)\chi^+(12,3)\Big\}.\end{aligned}\qquad(5)$$

Here F_0 and F_t denote the radial components of the wave function for the scattered electron which are associated with the initial and final states of the atom, respectively. The quantum numbers l_1' and m_1' refer to precollisional states of the target atom while l_1 and m_1 are to be associated with postcollisional states. The quantum numbers l_2', m_2', l_2, and m_2 provide a similar description of the pre- and postcollisional states of the scattering electron. We make use of the notation $\mathbf{r}_i=(r_i,\theta_i,\phi_i)=(r_i,\hat{r}_i)$ for the vector which gives the location of electron i relative to the helium nucleus. The spherical harmonics $Y_{lm}(i)=Y_{lm}(\hat{r}_i)$ and Clebsch-Gordan coefficients $C(l_1,l_2,l_3;m_1,m_2,m_3)$ are those defined by Rose.[17] Finally, the presence of the permutation operator $\sum_{\text{cyc}}$ in (5) ensures that $\Phi(123)$ will be antisymmetric with respect to the interchange of any pair of electrons.

We choose the polar axis to lie parallel to $\mathbf{k}_0$, the

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[12] P. M. Becker and J. S. Dahler, Phys. Rev. Letters **10**, 491 (1963).

[13] U. Fano, Phys. Rev. **135**, B863 (1964). We wish to thank J. W. Cooper and Dr. Fano for bringing this to our attention prior to publication.

[14] Reference 10, p. 233.

[15] H. Massey and B. L. Moiseiwitsch, Proc. Roy. Soc. (London) **A227**, 38 (1954).

[16] I. C. Percival and M. J. Seaton, Proc. Cambridge Phil. Soc. **53**, 654 (1957).

[17] M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957), Chap. 3, 4, App. 1, 3.

direction of the incident electron. From the criterion of cylindrical symmetry it then follows that m_2' is zero and so $M=m_1'+m_2'=m_1+m_2$ also vanishes. For the ^3P_g excited state with configuration $(2p)^2$ the value of l_1 is unity.

Although the function $\Phi(123)$ given by (5) is not an exact solution of the Schrödinger equation, it is suitable for use as a trial function in the Hulthén variation method. The application of this variation scheme provides a set of equations for the "optimal" Hartree-Fock radial functions F_0 and F_t. These equations are the same as those which one obtains by the following procedure:

(i) The trial function $\Phi(123)$ is substituted into the Schrödinger equation.

(ii) The resulting expression is premultiplied by one of the functions

$$[\chi^-(12,3)\psi_0(12)Y_{L0}(3)]^*$$

or

$$[\chi^+(12,3)\textstyle\sum_{m_2}C(l,l_2,L;-m_2,m_2,0)\psi_{-m_2}(12)Y_{l_2m_2(3)}]^*.$$

(iii) Integrations are performed over all coordinates of two electrons and over the angular and spin variables of the third. The performance of these operations leads to the *single* pair of coupled integrodifferential equations,

$$\left[\frac{d^2}{dr_3^2}-\frac{2}{r_3^2}+k_0^2+V_{00}(r_3)\right]F_0(r_3)+\int_0^\infty dr_1K_{00}(r_1,r_3)F_0(r_1)$$
$$=\int_0^\infty dr_1K_{t0}(r_1,r_3)F_t(r_1)\,,\quad (6a)$$

$$\left[\frac{d^2}{dr_3^2}-\frac{2}{r_3^2}+k^2+V_{tt}(r_3)\right]F_t(r_3)-\int_0^\infty dr_1K_{tt}(r_1,r_3)F_t(r_1)$$
$$=\int_0^\infty dr_1K_{0t}(r_1,r_3)F_0(r_1)\,.\quad (6b)$$

Here $F_0(r)\equiv F_0(r,l_2'=1)$ and $F_t(r)\equiv F_t\,(r,l_2=1)$ are the Hartree-Fock radial functions for the partial wave with $L=1$. It can be proved that no others contribute to the formation of the $(2p)^2\,{}^3P_g$ state. The functions $V_{00}(r)$ and $V_{tt}(r)$, which give rise to the so-called "direct distortions," are scattering potentials associated with the charge distributions of the atomic singlet and triplet states, respectively. Polarization of these distributions by the scattering electron has been neglected in the present investigation. The "exchange distortion" terms, in which the operators K_{00} and K_{tt} appear, provide the scattering potentials for elastic-exchange events. Finally, the kernels K_{0t} and K_{t0} account for the reactive process whereby exchange of the incident electron with one from the atom is accompanied by a singlet–triplet transition of the atomic state. Explicit expressions for all of these quantities are given in Appendix C.

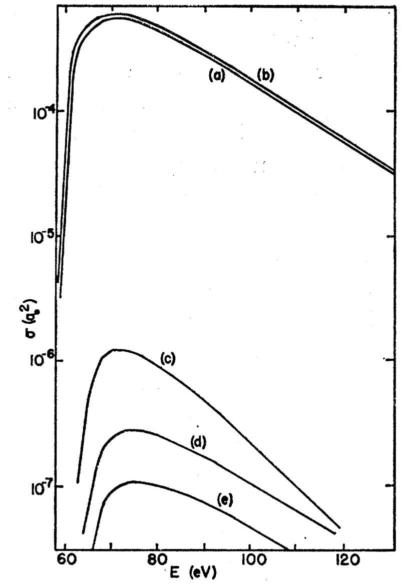

FIG. 2. Total cross sections in Born-Oppenheimer approximation for several states of helium. The cross sections are plotted against the energy of the incident electron. Curves (a) and (b) are both for the $(2p)^2\,{}^3P_g$ state, the former calculated with a two-screening-constant ground-state function, the latter with common values for the two screening constants. Curves (c), (d), and (e) are for the $2p3p\,{}^1P_g$, $2p3d\,{}^1D_u$ and $2p3d\,{}^3D_u$ states, respectively.

To fully characterize the functions F_0 and F_t we impose the familiar asymptotic boundary conditions,

$$F_0(r)\sim k_0^{-1/2}[e^{-i(k_0r-\pi/2)}-S(011;011)e^{i(k_0r-\pi/2)}],\quad (7a)$$

$$F_t(r)\sim k^{-1/2}[-S(111,011)e^{i(kr-\pi/2)}],\quad (7b)$$

where the coefficients $S(l_1,l_2,L;l_1'l_2',L)$ are elements of the scattering matrix. These coefficients are related to the S-matrix elements in the $(l_1m_1,l_2m_2;\,l_1'm_1',l_2'm_2')$ representation by the formulas,

$$S(l_1,m_1,l_2,m_2;l_1',m_1',l_2',m_2')$$
$$=\textstyle\sum_L\sum_M C(l_1,l_2,L;\,m_1,m_2,M)S(l_1,l_2,L;l_1',l_2',L)$$
$$\times C(l_1',l_2',L;\,m_1',m_2',M)\,.\quad (8)$$

The differential cross section for the excitation process then can be expressed in the form[6]

$$I(\theta,\phi)=(\pi/k_0^2)\textstyle\sum_{m_1}|\sum_{l_2m_2l_2'm_2'}\cdots\sum(2l_2'+1)^{1/2}i^{(l_2'-l_2)}$$
$$\times Y_{l_2m_2}(\theta,\phi)T(l_1,m_1,l_2,m_2;\,l_1',m_1',l_2',m_2')$$
$$\times\delta(l_2',1)\delta(l_2,1)\delta(m_1',\,0)|^2,\quad (9)$$

where $T(\alpha,\alpha')=\delta(\alpha,\alpha')-S(\alpha,\alpha')$ denotes an element of the T matrix. In the case before us here l_1' is equal to zero and the only nonvanishing elements of the T matrix are those for which $L=l_2=l_2'=1$. Therefore, the formula for the excitation cross section reduces to

$$I(\theta,\phi)=\pi k_0^{-2}\textstyle\sum_{m_1}|\sum_{m_2}\sqrt{3}Y_{lm_1}(\theta,\phi)$$
$$\times C(111;\,m_1,m_2,0)S(111,011)|^2$$
$$=(9/8k_0^2)|S(111;011)|^2\sin^2\theta.\quad (10)$$

In previous applications of the two-state theory it invariably has been found that an enormous number of partial waves contribute to the cross section. For example, in their calculations dealing with electron-impact excitation of the hydrogen atom, Burke and McCarroll[18] found it necessary to neglect contributions to the scattering process from an infinite number of angular momentum quantum numbers. Massey and Moiseiwitsch[9] had a similar experience in their study of singly-excited states of helium.

An additional complication was encountered in these two investigations when the theory was applied to nonspherical atomic states. Thus, for each choice of the total angular momentum L the Hartree-Fock equations coupled the component wave functions $F_0(r,l_2)$ for several values of l_2. The contrast is striking when one compares the complexities which faced those investigators to the relatively uninvolved situation before us here. This remarkable simplicity is a direct consequence of the fact that here the only angular momentum values involved are $L=l_2=l_2'=1$. The particularly unusual situation where only the incident and final p waves are involved occurs when the atomic wave function is approximated by a product of orbitals appropriate to a *single* atomic configuration, e.g., to the configuration $(2p)^2$ considered here. Instead, one might have chosen to represent the atomic wave function by a *finite* series of product orbitals, each pertaining to a different atomic configuration. He then would obtain in place of (6) the larger but still finite set of equations which characterize partial-wave contributions from additional channels. The associated elements of the scattering matrix would contribute a finite number of additional terms to the partial-wave expansion of the cross section. The entire spectrum of angular momenta becomes involved only if one were to introduce into the atomic wave function terms which were explicitly dependent upon the separation of the two electrons, e.g., functions of the Hylleraas type. From these comments it is clear that the simple structures of the cross section formula (10) and of the Eqs. (6) are due, at least in part, to the crude approximation we have used for the atomic wave function. However, in the other applications of the two-state theory to which we have referred, one finds that a vast number of partial waves contribute to the reaction cross section even when he uses the very simplest of single-configuration, product-orbital wave functions.

Numerical Procedure

The numerical technique we have adopted for solving the integrodifferential equations of interest to us here is based upon a procedure used previously by Burke *et al.*[19] to solve similar equations which they encountered in a study of electronic impact excitation of the $2s$ and $2p$ states of hydrogen. The method employs a Newton interpolation formula and is designed for solving equations of the general form $d^2F_l/dr^2=g_l(r,F_1,F_2,\cdots,F_n)$, $l=1,\ 2,\ \cdots n$. In the case of a single equation, $d^2F/dr^2=g(r,F)$, the solution is constructed according to the following prescription,

$$\begin{aligned} F(r_1)&=F(r_0)+hF'(r_0)+h^2(g_0-g_{-1})/6\,,\\ F(r_2)&=F(r_0)+2hF'(r_0)+h^2(2g_0+4g_1)/3\,, \qquad (11)\\ F'(r_2)&=F'(r_0)+h(g_0+4g_1+g_2)/3\,, \end{aligned}$$

where $F'=dF/dr$, $g_1=g[r_l,F(r_l)]$, $r_1=r_0+h$, and $r_2=r_0+2h$. Thus, if we have available $F(r_0)$, $F'(r_0)$, g_0, and g_{-1}, then we can calculate $F(r_1)$, g_1, $F(r_2)$, g_2, and $F'(r_2)$ in that order. Furthermore, we then have enough information to make a traverse of the next complete interval $\Delta r=2h$. The repeated use of this marching technique allows us to advance the integration to large values of r.

The integration is begun very near the origin where $(d^2/dr^2-2/r^2)F=0$ is an adequate approximation to both Eqs. (6). The solution which remains finite at the origin is given by $F=br^2$ where b denotes a constant. Therefore, the starting values are $F(0)=0$, $F'(0)=0$, $g_0=2b$, $F(-h)=bh^2$ and $g_{-1}=g[-h,F(-h)]$. In the numerical work the asymptotic boundary conditions (7) are more naturally expressed in terms of $rj_1(kr)$ where j_1 is the spherical Bessel function of first order. Thus, one begins near the origin with some assumed real value for the parameter b and proceeds with the integration until he reaches the asymptotic region. There the solution will be of the form $P[(kr)^{-1}\sin(kr+\delta)-\cos(kr+\delta)]$ with P the peak height of the cosine wave and δ a phase shift characteristic of the scattering process. At each point the integration procedure provides us with numerical values of F and F' so that the values of the two parameters P and δ can be calculated conveniently from the formulas,

$$\begin{aligned} P=\{F^2+[k^{-1}F'(1+k^{-2}r^{-2})+F(kr)^{-3}]^2\}^{1/2}&\\ \times[1+(kr)^{-2}]^{-1/2}, \qquad (12)&\\ \sin(kr+\delta)=(F'+r^{-1}F)/kP\,.& \end{aligned}$$

The remaining tasks are to adapt this integration technique to the problems of interest here and to establish the relationships between the solution parameters P and δ and the elements of the scattering matrix.

S-Matrix Elements

By the strong-coupling approximation we refer to the results which are obtained from a complete numerical solution of the Eqs. (6). One obtains the distorted-wave approximation by discarding from (6a) the term which

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[18] V. M. Burke and R. McCarroll, Proc. Phys. Soc. (London) **80**, 422 (1962).

[19] P. G. Burke, V. M. Burke, I. C. Percival, and R. McCarroll, Proc. Phys. Soc. (London) **80**, 413 (1962).

contains the operator K_{t0}. We shall distinguish between two different versions of the distorted-wave approximation; the DEW (distortion-plus-exchange) approximation in which only K_{t0} is set equal to zero and; the DW approximation wherein the terms of (6) containing K_{t0}, K_{00} and K_{tt} are neglected.

One can find many examples in the literature where the further approximation has been made of discarding from the potentials $V_{00}(r)$ and $V_{tt}(r)$ the terms which arise from the nonspherical characteristics of the excited atomic state. In order to obtain some estimate of the severity of this approximation we shall perform the DW calculations both with and without the nonspherical portions of the potentials.

Strong-Coupling Approximation

To indicate the method which we have used in this case the Eqs. (6) first are rewritten as

$$\left[\frac{d^2}{dr_3^2}-\frac{2}{r_3^2}+k_0^2+V_{00}(r_3)\right]F_0^{[n+1]}(r_3)$$

$$=\int_0^\infty dr_1[-K_{00}(r_1,r_3)F_0^{[n]}(r_1)+K_{t0}(r_1,r_3)F_t^{[n]}(r_1)], \qquad (13)$$

and

$$\left[\frac{d^2}{dr_3^2}-\frac{2}{r_3^2}+k^2+V_{tt}(r_3)\right]F_t^{[n+1]}(r_3)$$

$$=\int_0^\infty dr_1[K_{tt}(r_1,r_3)F_t^{[n]}(r_1)+K_{0t}(r_1,r_3)F_0^{[n]}(r_1)].$$

The iterative procedure is begun by setting $F_0^{[0]}$ and $F_t^{[0]}$ equal to zero. The resulting homogeneous ordinary differential equations for $F_0^{[1]}$ and $F_t^{[1]}$ are then solved by the numerical integration technique which we already have described. With these first-improved functions one next calculates and stores the exchange terms $\int_0^\infty dr_1[-K_{00}(r_1,r_3)F_0^{[1]}(r_1)+K_{t0}(r_1,r_3)F_t^{[1]}(r_1)]$ and $\int_0^\infty dr_1[K_{tt}(r_1,r_3)F_t^{[1]}(r_1)+K_{0t}(r_1,r_3)F_0^{[1]}(r_1)]$. The second step of the iteration is now clearly indicated. With n chosen equal to unity in (13) we solve this pair of inhomogeneous ordinary differential equations for $F_0^{[2]}$ and $F_t^{[2]}$. Further iterations are conducted until convergence of the solutions is achieved. For each step of this procedure we do, of course, use the same values for b_0 and b_t. In principle one could judge convergence by comparing successive solutions over the entire range of integration. However, it is highly desirable to adopt a more convenient measure of convergence. Thus, we compare the values of $F_\ell^{[n]}(r)$ and $F_\ell^{[n+1]}(r)$ at a few selected arguments, one being the end of the integration range, and when these differences fall within a prescribed tolerance say that convergence has been achieved. It required about ten such iterations for two successive solutions to agree within 0.01%.

The iterative procedure just described was used to construct solutions over the interval from zero to $25a_0$ in increments of $0.12a_0$. Then beginning at this point we changed to a smaller step size of $0.02a_0$ and continued the integration to $200a_0$. For such large arguments the actual solutions are numerically indistinguishable from their asymptotic forms and so the parameters δ_0, δ_t, P_0, and P_t can be accurately determined. Now although the exchange terms and the potentials V_{00} and V_{tt} are quite small near the outer end of the first interval, $(0,25a_0)$, they are not altogether negligible. Despite this fact we have completely neglected the exchange terms, $V_{00}(r)$, and all but the dominant $\mathcal{O}(r^{-3})$ portion of $V_{tt}(r)$ in conducting the integration from $25a_0$ to $200a_0$. To check the adequacy of this procedure we have continued the iterative solution beyond $25a_0$ to $35a_0$ and then at that point adopted the method for the asymptotic region. In all cases that we examined iterative solutions obtained on the intervals (0,25) and (0,35) agreed to within 0.01%. As an added check we have retained in a few cases the complete forms of V_{00} and V_{tt} over the final range of integration. The effect of this refinement was limited to the seventh decimal place of the solution parameters δ and P and the calculated cross section. Finally, to determine the influence of interval size upon the iterated solutions we have performed comparative DW and DEW calculations for values of h equal to $0.12a_0$, $0.08a_0$, and $0.04a_0$. The cross sections in the three cases differed by less than 1%.

The equations of the two-state theory have two independent solutions which are regular at the origin. These can be generated by performing the numerical integrations we have just described with two sets of constants, $(b_0^{(1)},b_t^{(1)})$ and $(b_0^{(2)},b_t^{(2)})$, which have been so chosen that the value of their determinant is nonzero. As Burke *et al.*[19] have mentioned the choice of a nonzero determinant for the b parameters does not guarantee that the solutions will be independent for large values of r. If the solutions are not sufficiently independent at large r then the accuracy of the calculated cross section will be effected. A check on the importance of this effect was made by constructing three "independent" solutions and comparing the cross sections calculated from all pairs. Generally the differences amounted to less than 5%, although there were a few calculated cross sections which differed by as much as 20%.

To calculate the cross section for excitation from two solutions with parameter sets $(\delta_0^{(1)},\delta_t^{(1)},P_0^{(1)},P_t^{(1)})$ and $(\delta_0^{(2)},\delta_t^{(2)},P_0^{(2)},P_t^{(2)})$ we construct the linear combinations of these solutions which satisfy the radiative boundary condition, (7). This is easily accomplished by multiplying each equation of the first set with $P_t^{(2)}e^{i\delta_t^{(1)}}$, each of the second set with $P_t^{(1)}e^{i\delta_t^{(2)}}$, and then subtracting the resulting expressions. The prescription for normalizations follows directly from a comparison of these solutions with the boundary conditions (7). The final result of these manipulations is the formula

$$|S(111;011)|^2=\frac{(2k/k_0)[P_t^{(1)}P_t^{(2)}]^2[1-\cos 2(\delta_t^{(1)}-\delta_t^{(2)})]}{[P_t^{(1)}P_0^{(2)}]^2+[P_t^{(2)}P_0^{(1)}]^2-2P_0^{(1)}P_0^{(2)}P_t^{(1)}P_t^{(2)}\cos(\delta_t^{(1)}-\delta_0^{(1)}-\delta_t^{(2)}+\delta_0^{(2)})}\,. \tag{14}$$

The differential cross section then can be calculated by inserting this expression into the formula (10).

Distorted-Wave Approximation

As we already have mentioned the basic step in this approximation is to discard from (6a) the inhomogeneous term involving K_{t0}. The resulting homogeneous integrodifferential equation,

$$\left[\frac{d^2}{dr_3^2}-\frac{2}{r_3^2}+k_0^2+V_{00}(r_3)\right]\tilde{F}_0(r_3)=-\int_0^\infty K_{00}(r_1,r_3)\tilde{F}_0(r_3)dr_1\,, \tag{15a}$$

can then be solved independently from the inhomogeneous equation,

$$\left[\frac{d^2}{dr_3^2}-\frac{2}{r_3^2}+k^2+V_{tt}(r_3)\right]\tilde{F}_t(r_3)=\int_0^\infty dr_1[K_{tt}(r_1,r_3)\tilde{F}_t(r_1)+K_{0t}(r_1,r_3)\tilde{F}_0(r_1)]\,, \tag{15b}$$

for the triplet function $\tilde{F}_t(r_3)$. To calculate the transition probability in this approximation it is only necessary to determine $\tilde{F}_0$ and $\mathfrak{F}_t$, where the latter denotes the solution of the homogeneous equation which is obtained by neglecting the second term on the right-hand side of (15b). Thus, if we subtract the product of $\tilde{F}_t$ with this homogeneous equation from the product of $\mathfrak{F}_t$ with (15b) and then integrate we obtain the formula,

$$\int_0^\infty dr[\mathfrak{F}_t(r)\tilde{F}_t''(r)-\tilde{F}_t(r)\mathfrak{F}_t''(r)]-\int_0^\infty\int_0^\infty drd\rho K_{tt}(r,\rho)[\tilde{F}_t(\rho)\mathfrak{F}_t(r)-\mathfrak{F}_t(\rho)\tilde{F}_t(r)]=\int_0^\infty\int_0^\infty drd\rho\mathfrak{F}_t(\rho)K_{0t}(r,\rho)\tilde{F}_0(\rho)\,. \tag{16}$$

The asymptotic boundary condition which we impose upon the solution of (15b) is given by

$$\mathfrak{F}_t(r)\sim k^{-1/2}\sin(kr-\tfrac{1}{2}\pi+\delta_t)e^{i\delta_t}. \tag{17}$$

The other boundary condition is that $\mathfrak{F}_t$ be zero at the origin.

Since K_{tt} is symmetric to the interchange of r and ρ [see Eq. (C5)], the integral containing this distortion term vanishes. Next we integrate the first term of (15) by parts and insert into that expression the asymptotic boundary conditions (7) and (17) and the boundary condition at the origin. The performance of these manipulations results in the formula

$$S(111;011)=\int_0^\infty\int_0^\infty drd\rho\mathfrak{F}_t(r)K_{0t}(r,\rho)\tilde{F}_0(\rho)\,, \tag{18}$$

for the S-matrix element. The differential cross section is obtained by inserting this expression into Eq. (10).

The functions $\mathfrak{F}_t$ and F_0 which appear in this formula must be correctly normalized. The solutions generated by our numerical procedure are proportional to the arbitrary scale parameters b_0 and b_t. By comparing the calculated peak height P_t to the normalization factor $k^{-1/2}$ in (17) we see that $\mathfrak{F}_t$ will be normalized properly if the values of the numerical solution are each multiplied by the factor $P_t^{-1}k^{-1/2}$. In the distorted-wave approximation the asymptotic form of the singlet wave function is given by

$$F_0(r)\sim-2ik_0^{-1/2}e^{i\delta_0}\sin(k_0r-\tfrac{1}{2}\pi+\delta_0)\,.$$

Therefore, our numerical solution must be multiplied by $2k_0^{-1/2}P_0^{-1}$ in order to ensure its proper normalization.

IV. DISCUSSION OF RESULTS

The results of our calculations and their implications are apparent from the accompanying figures. The curves of Fig. 3 permit us to evaluate the dependence of the cross sections in the DW approximation upon the choice of atomic ground-state wave functions and upon the noncentral portion of the triplet scattering potential. Thus, neglect of the noncentral term shifts the excitation curve to lower energy and increases its peak height. However, the effect upon the cross sections of a rather gross alteration in the atomic ground-state wave function is seen to be of very little consequence.

Figure 4 provides a comparison of the cross sections calculated from the BO, DW, DEW, and TS (two-state) approximations. In all cases the calculations were performed with the same one-parameter ground-state function. These are the most significant of our results since they illustrate the relative insensitivity of the calculated cross section to the choice of scattering theory. It is reasonable to expect that the predictions of the two-state theory are the most reliable. With this

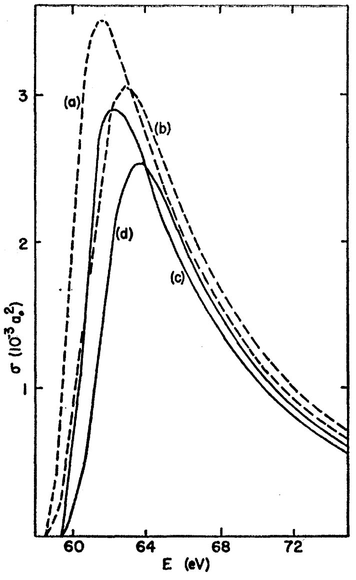

FIG. 3. Total cross sections in distorted-wave (DW) approximation. The cross section for excitation of the $(2p)^2\,{}^3P_g$ state of helium is plotted versus the energy of the incident electron. Curves (a) and (b) refer to calculations made with single-parameter ground-state wave functions while for (c) and (d) different screening constants were assigned to the two atomic electrons. For (a) and (c) only the spherical portion of the triplet potential V_{tt} was used. Curves (b) and (d) include the nonspherical parts of this potential.

as a standard we see that the DEW approximation fares very well, for its predictions are virtually indistinguishable from the two-state method. On the other hand, the DW approximation would appear to lead to a rather gross overestimate of the cross section. This is to be expected in the present case where the effects of exchange are so important.

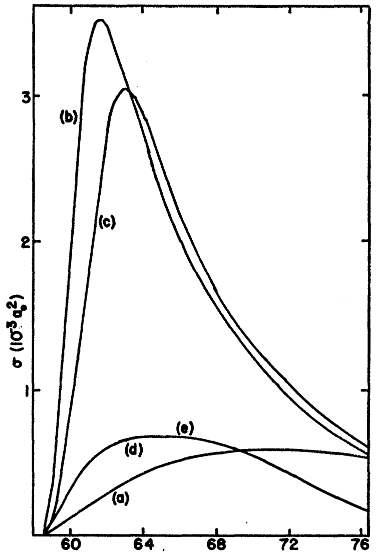

FIG. 4. Total cross sections for $(2p)^2\,{}^3P_g$ excitation calculated from the Born-Oppenheimer, distorted wave, and two-state strong-coupling theories. All of the calculations were performed using the same one-parameter ground-state wave function for helium. The various curves are (a) Born-Oppenheimer; (b) DW with spherical triplet potential, V_{tt}; (c) DW; (d) DEW and; (e) two state with strong coupling.

The most unexpected of our results is the close agreement which we find between the two-state and Born-Oppenheimer cross sections for it is well known that BO estimates are usually unreliable[9] for exchange processes which involve single-electron excitations. However, there is some previous evidence that the BO theory works rather better for (singlet S) → (triplet P) transitions than in other cases. Thus, in their study of the helium transition, $(1s)^2\,{}^1S \rightarrow (1s)(2p)\,{}^3P$, Massey and Moiseiwitsch found that the contribution to the cross section from the $L=1$ partial wave compensated somewhat for the gross overestimate of the BO theory for the $L=0$ partial wave. It should be emphasized, however, that neither of the individual BO partial cross sections agreed at all well with the corresponding terms of the strong-coupling theory.

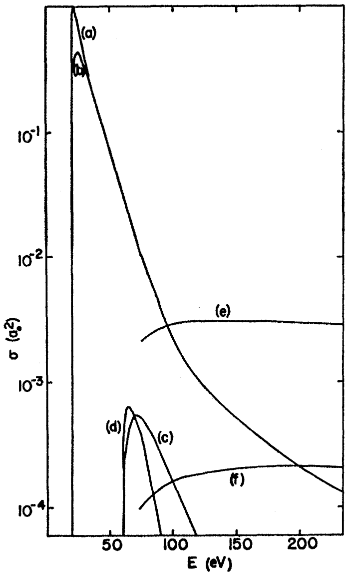

FIG. 5. Total cross sections for several states of helium as functions of the incident electron energy. This figure provides a comparison of the Born-Oppenheimer and the distorted-wave theories. The curves are (a) $1s2p\,{}^3P_u$, Born-Oppenheimer (see Ref. 9); (b) $1s2p\,{}^3P_u$, DEW (see Ref. 9); (c) $(2p)^2\,{}^3P_g$, Born-Oppenheimer; (d) $(2p)^2\,{}^3P_g$, DEW; (e) $2s2p\,{}^1P_u$, Born-Oppenheimer (see Ref. 20); and (f) $2s2p\,{}^1P_u$, Born-Oppenheimer (see Ref. 20).

We have included in Fig. 5 the BO and DEW cross sections for the electronic impact excitation of the $1s2p\,{}^3P_u$ state of helium,[9] as well as the Born approximation predictions of Massey and Mohr[20] for several autoionizable levels. Although the reliability of these latter results is open to question they have been presented here for purposes of comparison.

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[20] H. S. W. Massey and C. B. O. Mohr, Proc. Cambridge Phil. Soc. 31, 604 (1935).

The results of our calculations have encouraged us greatly, since there are clear indications that the uncomplicated Born-Oppenheimer theory may emerge as a reliable method for calculating the cross sections for excitation of anomalous states—provided that the product form is a good approximation for the excited-state wave functions. A complete verification of this conjecture requires that a few more special cases be examined, the most obvious candidates being the alkaline earths Be, Mg, Ca, etc. Provided that one neglects the effects of excitation upon the core electrons of these atoms, the theory presented here can be applied almost without change to processes such as the transition from Be $(1s)^2(2s)^2\,{}^1S_g$ to Be $(1s)^2(2p)^2\,{}^3P_g$ or Be $(1s)^2(2p)(3p)\,{}^3P_g$. Furthermore, anomalous states of the alkaline earths are of intrinsic interest, since there is ample spectroscopic evidence for their existence, and since it has been assumed in the past that these states could not be excited by impact of a single electron.[21] Born-Oppenheimer cross sections for the two beryllium excitation processes mentioned above are given in Appendix E.

ACKNOWLEDGMENTS

We wish to thank the National Science Foundation for partial support of this research. We are also indebted to the staff of the Numerical Analysis Center of the University of Minnesota for use of the Control Data Corporation 1604 computer and for assistance in the solution of this problem.

APPENDIX A: ATOMIC WAVE FUNCTIONS AND ENERGIES

To calculate cross sections from the formulas given in the preceding sections it is first necessary to make explicit choices for the atomic wave functions and to determine the associated energy eigenvalues. We have constructed approximate atomic wave functions from properly symmetrized products of hydrogenic orbitals. The values for the screening constants were chosen to minimize the energy. These calculations were performed for the states $(1s)^2\,{}^1S_g$, $(2p)^2\,{}^3P_g$, $2p3p\,{}^1P_g$, $2p3d\,{}^1D_u$, and $2p3d\,{}^3D_u$, each of which is the least energetic of its symmetry type. Therefore, the energy eigenvalues calculated from the trial functions are necessarily upper bounds to the exact values.

The wave function for the ground state is given by

$$\psi_0=N[\psi_{100}(\alpha,1)\psi_{100}(\beta,2)+\psi_{100}(\alpha,2)\psi_{100}(\beta,1)],$$

$$N^{-2}=2\left\{1+\left[\int d\mathbf{r}\psi_{100}(\alpha,r)\psi_{100}(\beta,r)\right]^2\right\}, \tag{A1}$$

which, in the special case of $\alpha=\beta$, reduces to $\psi_{100}(\alpha,1)\times\psi_{100}(\beta,2)$.

The approximate wave functions which we have used for the other states are

$$(2p)^2\,{}^3P_g:\psi_m=\sum_\nu C(1,1,1;\nu,m-\nu,m)\times\psi_{21\nu}(\gamma,1)\psi_{21,m-\nu}(\gamma,2), \tag{A2}$$

$$2p3p\,{}^1P_g:\psi_m=2^{-1/2}\sum_\nu C(1,1,1;\nu,m-\nu,m)\times[\psi_{21\nu}(\gamma,1)\psi_{31,m-\nu}(\delta,2)+\psi_{21\nu}(\gamma,2)\psi_{31,m-\nu}(\delta,1)], \tag{A3}$$

$$2p3d\,{}^1D_u:\psi_m=2^{-1/2}\sum_\nu C(1,2,2;\nu,m-\nu,m)\times[\psi_{21\nu}(\gamma,1)\psi_{32,m-\nu}(\delta,2)+\psi_{21\nu}(\gamma,2)\psi_{32,m-\nu}(\delta,1)], \tag{A4}$$

$$2p3d\,{}^3D_u:\psi_m=2^{-1/2}\sum_\nu C(1,2,2;\nu,m-\nu,m)\times[\psi_{21\nu}(\gamma,1)\psi_{32,m-\nu}(\delta,2)-\psi_{21\nu}(\gamma,2)\psi_{32,m-\nu}(\delta,1)], \tag{A5}$$

where the atomic orbitals are given by

$$\psi_{nlm}(\mathbf{r})=R_{nl}(r)Y_{lm}(\hat{r}).$$

Here the symbols α, β, γ, and δ denote screening constants and the R_{nl} are hydrogenic radial functions.

$$R_{10}(\alpha,r)=2\alpha^{3/2}e^{-\alpha r},$$
$$R_{21}(\gamma,r)=(\gamma^5/24)^{1/2}re^{-\gamma r/2},$$
$$R_{31}(\delta,1)=(8\delta^5/19683)^{1/2}r(6-\delta r)e^{-\delta r/3},$$
$$R_{32}(\delta,r)=(8\delta^7/98415)r^2e^{-\delta r/3}.$$

The expectation value for the energy of the $2p3p\,{}^1P_g$ state is given by

$$E=\tfrac{1}{4}\gamma(\gamma-4)+\tfrac{1}{9}\delta(\delta-4)+I_1+I_2+I_3,$$

where

$$I_1=(4\delta/27)\{\tfrac{3}{2}-(\delta/\gamma)^2+(16\delta^2/243\gamma^2D^2)[18(1+2\gamma/D+2\gamma^2/D^2+\gamma^3/D^3)-(6\delta/D)(2+6\gamma/D+8\gamma^2/D^2+5\gamma^3/D^3)+(\gamma^2/D^2)(3+12\gamma/D+20\gamma^2/D^2+15\gamma^3/D^3)]\},$$

$$I_2=(1024\gamma^5\delta^5/2187D^9)(-126+378\delta/D-289\delta^2/D^2),$$

$$I_3=(131072\gamma^5\delta^5/2187D^{12})\times[2(3\gamma^2-\tfrac{4}{3}\delta^2)-\gamma\delta(3\gamma-\tfrac{4}{3}\delta)](\gamma-\delta).$$

Here $D=\gamma+\tfrac{2}{3}\delta$. For the $2p3d\,{}^1D_u$ and $2p3d\,{}^3D_u$ states

$$E=\tfrac{1}{4}\gamma(\gamma-4)+\tfrac{1}{9}\delta(\delta-4)+I_1\pm I_2,$$

where the + and − signs are to be associated with the

TABLE I. Energy eigenvalues for several states of helium.

State	Screening constants	Energy (Ry)	Energy (eV above true ground)
$(1s)^2\,{}^1S_g$	2.18316, 1.18854	−5.75132	0.77
$(1s)^2\,{}^1S_g$	1.6875	−5.69531	1.53
$(2p)^2\,{}^3P_g$	1.67188	−1.39758	59.98
$2p3p\,{}^1P_g$	1.84592, 1.73328	−1.14195	63.46
$2p3d\,{}^1D_u$	1.96419, 1.19537	−1.12328	63.71
$2p3d\,{}^3D_u$	1.99226, 1.05763	−1.11655	63.80

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[21] G. Herzberg, *Atomic Spectra and Atomic Structure* (Dover Publications, Inc., New York, 1944), Chap. 4, p. 165.

TABLE II. Energy eigenvalues predicted for the $(2p)^2\,{}^3P_g$ state.

Method	Energy (Ry)	Energy (eV above true ground)
One-parameter hydrogenic orbital	−1.39758	59.98
Two-parameter hydrogenic[a]	−1.3976	59.98
Self-consistent field[b]	−1.4018	59.93
Hydrogenic orbitals with[c] slight corrections	−1.4074	59.85
Extended Fock method[d]	−1.4082	59.84
Correlation[e]	−1.4109	59.80
Correlation[f]		59.73
Configuration interaction[g]	−1.42021	59.68
"Experimental"[h]		59.67

[a] T.-Y. Wu and S. T. Ma, Phys. Rev. **48**, 917 (1935).

[b] W. S. Wilson, Phys. Rev. **48**, 536 (1935).

[c] T.-Y. Wu and S. T. Shen, Chinese J. Phys. **5**, 150 (1944).

[d] K. K. Eringis, P. Sh. Fridberg, and V. K. Shugurov, Opt. i Spektroskopiya **11**, 297 (1961) [English transl.: Opt. Spectry. (USSR) **11**, 161 (1961)].

[e] T.-Y. Wu, Phys. Rev. **66**, 291 (1944).

[f] M. J. S. Dewar and A. L. Chung, J. Chem. Phys. **39**, 1741 (1963).

[g] E. Holøien, J. Chem. Phys. **29**, 676 (1958).

[h] This value is obtained from the sum of the energies of the $1s2p\,{}^3P_u$ state and the 320.38 Å emission line. See W. C. Martin, J. Res. Natl. Bur. Std. **A64**, 19 (1960).

singlet and triplet states, respectively, and where

$$I_1=(\delta/45)\{10-\tfrac{4}{3}\delta^2/\gamma^2+(64\delta^6/729\gamma^2D^4)\times[3+12\gamma/D+20\gamma^2/D^2+15\gamma^3/D^3]\},$$

$$I_2=-11484\gamma^5\delta^7/3645D^{11}.$$

The values for the screening constants and the energy eigenvalues for these states are presented in Table I.

Table II provides a summary of the several calculations for the $(2p)^2\,{}^3P_g$ state which have appeared in the literature.

APPENDIX B: THE J FUNCTIONS OF THE BORN-OPPENHEIMER APPROXIMATION

The functions J_i which appear in the formulas (4) for the Born-Oppenheimer scattering amplitudes are given by

$$J_1=4\gamma k_0(k_0^2+\tfrac{1}{4}\gamma^2)^{-3},$$

$$J_3=8k_0\delta(3k_0^2-\tfrac{1}{3}\delta^2)(k_0^2+\tfrac{1}{9}\delta^2)^{-4},$$

$$J_5=16\delta k_0^2(k_0^2+\tfrac{1}{9}\delta^2)^{-4},$$

$$J_2=3[\mathcal{B}^{-5}J_7(\alpha/k;\mathcal{B}/k)+\mathcal{A}^{-5}J_7(\beta/k,\mathcal{A}/k)],$$

$$J_4=3\{B^{-5}[(6-5\delta/B)J_7(\alpha/k,B/k)+\delta B^{-1}J_8(\alpha/k,B/k)]+A^{-5}[(6-5\delta/A)J_7(\beta/k,A/k)+\delta A^{-1}J_8(\beta/k,A/k)]\},$$

$$J_6=5[B^{-7}J_9(\alpha/k,B/k)+A^{-7}J_9(\beta/k,A/k)],$$

where

$$A=\alpha+\tfrac{1}{3}\delta,\quad B=\beta+\tfrac{1}{3}\delta,\quad \mathcal{A}=\alpha+\tfrac{1}{2}\gamma,\quad \mathcal{B}=\beta+\tfrac{1}{2}\gamma,$$

and

$$J_7(\alpha,B)=-8\alpha[\mathrm{ctn}^{-1}\alpha-\mathrm{ctn}^{-1}(\alpha+B)]+8B[\alpha S+B(\alpha+B)^2S^2-B^2(\alpha+B)S^3],$$

$$J_8(\alpha,B)=B^3k^{-1}[-3S'+(3B-\alpha)S''+B(B+\alpha)S'''],$$

$$kJ_9(\alpha,B)=-72\alpha(1+\alpha^2)[\mathrm{ctn}^{-1}\alpha-\mathrm{ctn}^{-1}(\alpha+B)]+\tfrac{1}{2}(g_0S-g_1S'+g_2S''-g_3S'''+g_4S''''),$$

and

$$S=[(\alpha+B)^2+1]^{-1},$$

$$S'=dS/d(\alpha+B),$$

$$g_0=144\alpha B(1+\alpha^2),$$

$$g_1=72\alpha B^2(1+\alpha^2)+12B^5,$$

$$g_2=24\alpha B^3(1+\alpha^2)+12B^5(B-\alpha),$$

$$g_3=6\alpha B^4(1+\alpha^2)+B^5(1+3\alpha^2-12\alpha B-9B^2),$$

$$g_4=\alpha B^5(1+\alpha^2)+B^6(1+3\alpha^2+3\alpha B+B^2).$$

APPENDIX C: OPERATORS FROM THE HARTREE-FOCK EQUATIONS

The operators V_{00} and K_{00} for the incident channel are given by

$$V_{00}(r)=4N^2r^{-1}\{(1+\alpha r)e^{-2\alpha r}+(1+\beta r)e^{-2\beta r}+64\alpha^3\beta^3(\alpha+\beta)^{-6}[2+(\alpha+\beta)r]e^{-(\alpha+\beta)r}\},\quad\text{(C1)}$$

and (for the special choice of screening constants $\alpha=\beta$),

$$K_{00}(r_1,r_2)=(8/3)\alpha^3r_1r_2(r_</r_>^2)_{12}e^{-\alpha(r_1+r_2)}.\quad\text{(C2)}$$

The function $(r_</r_>^2)_{12}$ is equal to r_1/r_2^2 when $r_1<r_2$ and to r_2/r_1^2 when $r_1>r_2$.

The triplet-state potential V_{tt} is given by,

$$V_{tt}(r)=4r^{-1}e^{-\gamma r}\left(1+\frac{3}{4}\gamma r+\frac{1}{4}\gamma^2r^2+\frac{1}{24}\gamma^3r^3\right)-T(r),\quad\text{(C3)}$$

where

$$T(r_3)\equiv\int_0^\infty r_1^2dr_1\int_0^\infty r_2^2dr_2[R_{21}(r_1)R_{21}(r_2)]^2(r_<^2/r_>^3)_{13}$$
$$=2\gamma^{-2}r_3^{-3}\left[6-e^{-\gamma r_3}\left(6+6\gamma r_3+3\gamma^2r_3^2+\gamma^3r_3^3+\frac{1}{4}\gamma^4r_3^4+\frac{1}{24}\gamma^5r_3^5\right)\right]\quad\text{(C4)}$$

denotes the contribution which is due to the nonspherical part of the atomic wave function. The triplet exchange operator may be expressed in the form,

$$K_{tt}(r_1,r_2)=\frac{1}{24}\gamma^5r_1^2r_2^2e^{-1/2\gamma(r_1+r_2)}\{-\tfrac{1}{2}[E+\gamma(1+\tfrac{1}{4}\gamma)+2(1-\gamma)(r_1^{-1}+r_2^{-1})]-Q(r_1)-Q(r_2)+(1/r_>)_{12}+\tfrac{2}{5}(r_<^2/r_>^3)_{12}\}\quad\text{(C5)}$$

with

$$Q(r)=\gamma^{-2}r^{-3}[6-e^{-\gamma r}(6+6\gamma r+2\gamma^2r^2+\tfrac{1}{4}\gamma^3r^3)].\quad\text{(C6)}$$

Finally, the exchange-interaction operators K_{0t} and

K_{t0} are defined by

$$K_{0t}(r_1,r_2)=-K_{t0}(r_2,r_1)=-\gamma^5N(\alpha^3\beta^3/3)^{1/2}r_1^2r_2^{-1}e^{-\gamma r_1}/2$$
$$\times\{\mathcal{B}^{-5}e^{-\alpha r_2}[8-e^{-\mathcal{B}r_2}(8+8\mathcal{B}r_2+4\mathcal{B}^2r_2^2+\mathcal{B}^3r_2^3)]$$
$$+\mathcal{A}^{-5}e^{-\beta r_2}[8-e^{-\mathcal{A}r_2}(8+8\mathcal{A}r_2+4\mathcal{A}^2r_2^2+\mathcal{A}^3r_2^3)]\}\quad\text{(C7)}$$

with $\mathcal{A}=\alpha+\frac{1}{2}\gamma$ and $\mathcal{B}=\beta+\frac{1}{2}\gamma$.

APPENDIX D: DIRECT EXCITATION PROCESSES

It already has been established that the Born direct scattering amplitude f_{dm} vanishes for the excitation of doubly-excited states which are stable to autoionization. Here we shall prove that the contribution to the excitation process from direct scattering vanishes in the two-state theory as well and that this result is true for a large class of atomic trial functions.

Previously we have developed the two-state theory only for excitation of the $(2p)^2\,{}^3P_g$ state, and consequently the only reactive terms which appeared in (6) were those involving the exchange-interaction operators K_{0t} and K_{t0}. To study the excitation of singlet states we replace the trial function (5) with

$$\Phi(123)=\sum_{\text{cyc}}\{\psi_0(12)Y_{L0}(3)r_3^{-1}F_0(r_3,L)\chi^-(12,3)$$
$$+\sum_{l_2''}\sum_{m_2''}C(l_1,l_2'',L;-m_2'',m_2'',0)\psi_{-m_2''}(12)$$
$$\times Y_{l_2''m_2''}(3)r_3^{-1}F_s(r_3,l_2'')\chi^-(12,3)\}\quad\text{(D1)}$$

and then construct the integrodifferential equations for the Hartree-Fock functions F_0 and F_s according to the prescription given in Sec. III. When this is done one discovers that the excitation will occur only if coupling terms such as

$$C_f=\sum_{m_2}C(l_1,l_2,L;-m_2,m_2,0)$$
$$\times\int\int\int d\mathbf{r}_1d\mathbf{r}_2d\hat{r}_3\psi_{-m_2}^*(12)Y_{l_2m_2}^*(3)$$
$$\times(H-E)\psi_0(12)Y_{L0}(3)r_3^{-1}F_0(r_3,L)\quad\text{(D2)}$$

are different from zero.

We can approximate the ground-state wave function very accurately with the linear combination of S-state configurations,

$$\psi_0(12)=\sum_{n_cl_cm_cn_dl_dm_d}\cdots\sum a_{n_cl_cn_dl_d}R_{n_cl_c}(1)R_{n_dl_d}(2)$$
$$\times C(l_cl_d,0;m_c,m_d,0)Y_{l_cm_c}(1)Y_{l_dm_d}(2).\quad\text{(D3)}$$

Similarly, the wave function for the excited state can be written as the superposition of l_1 configurations,

$$\psi_m(12)=\sum_{n_al_an_bl_b\nu}\cdots\sum b_{n_al_an_bl_b}R_{n_al_a}(1)R_{n_bl_b}(2)$$
$$\times C(l_a,l_b,l_1;\nu,m-\nu,m)Y_{l_a\nu}(1)Y_{l_b,m-\nu}(2),\quad\text{(D4)}$$

each of which has the same parity. The sets of quantum numbers $n_\alpha l_\alpha m_\alpha$ specify the states of orbital electrons and the functions $R_{nl}(r)$ are characteristic of the electronic radial distributions. Finally, the values of the scalar coefficients $a_{nln'l'}$ and $b_{nln'l'}$ (which could be determined by a variation method) are indicative of the relative importances of the various configurations to the wave functions for the states in question.

In terms of these mixed-configuration approximations for the atomic wave functions the direct-excitation term C_f may be written as

$$C_f=\sum_{n_an_bn_cn_dl_al_bl_cl_d}\cdots\sum b_{n_al_an_bl_b}^*a_{n_cl_cn_dl_d}\int_0^\infty dr_1r_1^2\int_0^\infty dr_2r_2^2$$
$$\times R_{n_al_a}^*(1)R_{n_bl_b}^*(2)R_{n_cl_c}(1)R_{n_dl_d}(2)$$
$$\times[C_{00}-2(C_{12}+C_{13}+C_{23})],\quad\text{(D5)}$$

where

$$C_{00}=G_{n_an_b\cdots l_d}(r_1,r_2,r_3)\delta(l_1,0)\delta(l_2,L)$$
$$\times\delta(l_a,l_b)\delta(l_b,l_c)\delta(l_c,l_d),\quad\text{(D6)}$$

$$C_{12}=\{(-1)^{l_a+l_c}[(2l_a+1)/(2l_c+1)]^{1/2}$$
$$\times\sum_{l\geq0}(r_<^l/r_>^{l+1})_{12}C(l,l_a,l_b;0,0,0)^2\}$$
$$\times\delta(l_1,0)\delta(l_2,L)\delta(l_a,l_b)\delta(l_c,l_d),\quad\text{(D7)}$$

and where

$$C_{j3}=\{[(2l_2+1)/(2l_1+1)(2L+1)]^{1/2}(r_<^{l_1}/r_>^{l_1+1})_{j3}$$
$$\times C(l_1,l_2,L;0,0,0)C(l_1,l_b,l_a;0,0,0)\}$$
$$\times\delta(l_j',l_c)\delta(l_c,l_d),\quad\text{(D8)}$$

for $j=1$, 2. Here $l_1'\equiv l_b$ and $l_2'=l_a$. The precise functional form of $G_{n_an_b\cdots l_d}(r_1,r_2,r_3)$ is of no consequence to us here.

Now if a doubly-excited state is to be stable to autoionization, its symmetry must differ from that of every adjacent continuum state. However, there exist continuum states with all values of the orbital and spin angular momentum. Consequently the parities of stable doubly-excited states must be different from those of all continuum states with similar energies and with identical values of the spin and orbital angular momentum. If the energy of the anomalous state exceeds the value of 65.23 eV, which is required for production of the He$^+(2p)$ ionic specie, this criterion can not be satisfied. The reason is that beyond this limit there are continuum states with both even and odd parity for every value of the angular momentum. For energies beneath this threshold the parity of a stable doubly-excited state with angular momentum l_1 must differ from the parities of all continuum states with wave functions of the form,

$$\psi_{\mathbf{k}l_1m_1}(12)=2^{-1/2}[R_{10}(1)\mathcal{R}_{\mathbf{k}l_1}(2)Y_{00}(1)Y_{l_1m_1}(2)$$
$$+R_{10}(2)\mathcal{R}_{\mathbf{k}l_1}(1)Y_{00}(2)Y_{l_1m_1}(1)].$$

Here $\mathcal{R}_{\mathbf{k}l_1}(i)$ denotes the radial portion of the wave function for an unbound electron with a force-free propagation vector $\mathbf{k}$.

In order that a doubly-excited state with the wave function given by (D4) be stable to autoionization the parities $(-1)^{l_a+l_b}$ and $(-1)^{l_1}$ must be different, i.e., $l_a+l_b+l_1$ must be an odd integer. However, from (D6)–(D8) it follows that each of the functions C_{00}, C_{12}, C_{13}, and C_{23} will vanish unless this same integer $l_a+l_b+l_1$ is even. The basis for this conclusion is immediately obvious in the cases of C_{00} and C_{12}; with C_{13} and C_{23} it follows from the fact that $C(l_1,l_2,l_3;0,0,0)$ equals zero unless $l_1+l_2+l_3$ is even. These observations establish that direct scattering does not contribute to impact excitation of stable, doubly-excited singlet states.

APPENDIX E: BORN-OPPENHEIMER CROSS SECTIONS FOR TWO LOW-LYING STATES OF BERYLLIUM

We have mentioned at the close of Sec. IV that there is available a considerable amount of spectroscopic information concerning the anomalous states of beryllium. The least energetic of these, a ${}^3P_g$ state with the configuration $(1s)^2(2p)^2$, is located well below the first ionization potential. The next of the ${}^3P_g$ states has the configuration $(1s)^2 2p3p$ and an energy roughly 1.7 eV above the ionization potential. Since Herzberg[21] has reported that the observed emission line for the transition $(1s)^2(2p)^2\,{}^3P_g \rightarrow (1s)^2 2s2p\,{}^3P_u$ is quite intense, there must exist some very effective process for producing atoms in this anomalous ${}^3P_g$ state. Herzberg concluded that this excitation process was not the result of the collision of a single electron but that it proceeded "through the $sp\,{}^3P$ state by two successive electron collisions." To us this explanation seems unlikely since the radiative lifetimes of the postulated intermediate states are probably no greater than 10^{-7} sec. Furthermore, the results presented below indicate that the single-shot mechanism for production of anomalous states is very efficient—so much so that it almost certainly overshadows the Herzberg mechanism in importance.

We have assumed that configuration interaction can be neglected in constructing approximate product-orbital wave functions for the various states of beryllium. The basic orthonormal hydrogenic orbitals which we have used are

$$\psi_{1s}(\mathbf{r}) = 2\alpha^{3/2}e^{-\alpha r}Y_{00}(\hat{r}),$$
$$\psi_{2s}(\mathbf{r}) = N[u_{2s}(\mathbf{r})-\lambda\psi_{1s}(\mathbf{r})],$$

with

$$u_{2s}(\mathbf{r}) \equiv (\beta^3/2)^{1/2}(1-\beta r/2)e^{-\beta r/2}Y_{00}(\hat{r}),$$
$$\lambda \equiv 2(2\alpha^3\beta^3)^{1/2}(\alpha-\beta)(\alpha+\beta/2)^{-4},$$
$$N \equiv (1-\lambda^2)^{-1/2},$$

and

$$\psi_{21\nu}(\mathbf{r}) = (\gamma^5/24)^{1/2} r e^{-\gamma r/2}Y_{1\nu}(\hat{r}),$$
$$\psi_{31\nu}(\mathbf{r}) = (8\gamma^5/3^9)^{1/2} r(6-\gamma r)e^{-\gamma r/3}Y_{1\nu}(\hat{r}).$$

In accordance with the suggestions of Morse, Young, and Haurwitz[22] and of Duncanson and Coulson,[23] we have chosen $\alpha=3.7$, $\beta=2.0$ and $\gamma=1.75$. Variation calculations we performed for the $2p3p\,{}^1P_g$ state of helium indicated that the screening constants for the two electrons were very nearly equal. This provides some justification for our present use of the same screening constant γ for the $\psi_{21\nu}$ and $\psi_{31\nu}$ orbitals. With these wave functions the energies for the ground state and for the lower lying of the two excited states are -29.1575 and -28.6431 Ry, respectively. The difference of 0.5144 Ry or 7.1 eV agrees fairly well with the experimental value of 7.3 eV. For the energy of the $(1s)^2 2p3p\,{}^3P_g$ state we have adopted the experimental value of 0.808 Ry or 11.0 eV above ground. This state is imbedded within the first ionization continuum of the beryllium atom.

The scattering amplitudes of the Born-Oppenheimer approximation are given by

$$f_m(\theta,\phi;(2p)^2)$$
$$=\frac{1}{4\pi}\sum\nolimits_\nu C(1,1,1;\nu,m-\nu,m)\int\int\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 e^{-i\mathbf{k}\cdot\mathbf{r}_3}$$
$$\times\psi_{21\nu}^*(1)\psi_{21m-\nu}^*(2)(2/r_{23})e^{i\mathbf{k}_0\cdot\mathbf{r}_1}\psi_{2s}(2)\psi_{2s}(3), \quad \text{(E1)}$$

and

$$f_m(\theta,\phi;2p3p)$$
$$=\frac{2^{-1/2}}{4\pi}\sum\nolimits_\nu C(1,1,1;\nu,m-\nu,m)\int\int\int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 e^{-i\mathbf{k}\cdot\mathbf{r}_3}$$
$$\times[\psi_{21\nu}^*(1)\psi_{31m-\nu}^*(2)-\psi_{21\nu}^*(2)\psi_{31m-\nu}^*(1)]$$
$$\times(2/r_{23})e^{i\mathbf{k}_0\cdot\mathbf{r}_1}\psi_{2s}(2)\psi_{2s}(3). \quad \text{(E2)}$$

Just as in the case of helium the components with $m=0$ vanish and $|f_1|=|f_{-1}|$. Therefore, the differential cross sections are related to the scattering amplitudes by the formula $I(\theta,\phi)=3(2k/k_0)|f_1(\theta,\phi)|^2$.

The task of performing the multiple integrals is tedious but straightforward. The results are

$$f_1(\theta,\phi;(2p)^2)$$
$$=2N^2k_0\gamma^6\Big\{(k_0^2+\gamma^2/4)^{-3}$$
$$\times\int_0^\infty dr\,j_1(kr)G_1(r)\Big\}\sin\theta e^{i\phi}, \quad \text{(E3)}$$

and

$$f_1(\theta,\phi;2p3p)$$
$$=2^{1/2}(8/81)N^2k_0\gamma^6\Big\{6(k_0^2-\gamma^2/9)(k_0^2+\gamma^2/9)^{-4}$$
$$\times\int_0^\infty dr\,j_1(kr)G_1(r)+(k_0^2+\tfrac{1}{4}\gamma^2)^{-3}$$
$$\times\int_0^\infty dr\,j_1(kr)G_2(r)\Big\}\sin\theta e^{i\phi}, \quad \text{(E4)}$$

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[22] P. M. Morse, L. A. Young, and E. S. Haurwitz, Phys. Rev. **48**, 1948 (1935).

[23] W. E. Duncanson and C. A. Coulson, Proc. Roy. Soc. Edinburgh **A62**, 37 (1944).

where

$$G_1(r)=[(1-r)e^{-r}-\lambda\alpha^{3/2}e^{-\alpha r}][B^{-5}\{8-e^{-Br}(8+8Br+4B^2r^2+B^3r^3)\}$$
$$-B^{-6}\{40-e^{-Br}(40+40Br+20B^2r^2+6B^3r^3+B^4r^4)\}-\lambda\alpha^{3/2}A^{-5}\{8-e^{-Ar}(8+8Ar+4A^2r^2+A^3r^3)\}], \quad \text{(E5)}$$

and

$$G_2(r)=3[(1-r)e^{-r}-\lambda\alpha^{5/2}e^{-\alpha r}][-D^{-5}\{24-e^{-Dr}(24+24Dr+12D^2r^2+4D^3r^3+D^4r^4)\}$$
$$-D^{-6}\{280-e^{-Dr}(280+280Dr+140D^2r^2+44D^3r^3+9D^4r^4+D^5r^5)\}$$
$$+D^{-7}\{240-e^{-Dr}(240+240Dr+120D^2r^2+38D^3r^3+8D^4r^4+D^5r^5)\}$$
$$+\lambda\alpha^{3/2}C^{-5}\{24-e^{-Cr}(24+24Cr+12C^2r^2+4C^3r^3+C^4r^4)\}$$
$$-\lambda\alpha^{5/2}C^{-6}\{40-e^{-Cr}(40+40Cr+20C^2r^2+6C^3r^3+C^4r^4)\}]. \quad \text{(E6)}$$

In these formulas, $A=\alpha+\frac{1}{2}\gamma$, $B=1+\frac{1}{2}\gamma$, $C=\alpha+\frac{1}{3}\gamma$, and $D=1+\frac{1}{3}\gamma$. The screening parameter β does not appear since it has been replaced everywhere by its numerical value 2. Although the integrals involving the spherical Bessel functions $j_1(x)$ and the functions $G_1(x)$ and $G_2(x)$ can be performed analytically, the resulting expressions are extremely complicated. In fact, we found it less difficult to directly program these integrals for numerical integration than to program the very involved algebraic expressions which are obtained from analytical integration.

The calculated values for the total cross sections,

$$\sigma=\int_0^{2\pi}d\phi\int_0^{\pi}d\theta\,\sin\theta I(\theta,\phi)=(16\pi k/k_0)\,|f_1(\tfrac{1}{2}\pi,0)|^2,$$

are illustrated in Fig. 6. The most striking features of these results are, of course, the enormous magnitudes of the cross sections. Thus, according to the BO approximation, the probability of producing a doubly-excited state is comparable to that of causing an ordinary single-electron excitation. The great disparity in size between the cross sections for helium and beryllium is due to the strong overlap of the $2s$ and $2p$ orbitals in beryllium and to the most negligible overlap of the $1s$ and $2p$ orbitals in helium. From a comparison of curves (a) and (c) of Fig. 3 one sees that a similar disparity, amounting again to approximately three orders of magnitude, separates the magnitudes of the cross sections for excitation of the $(2p)^2$ and $2p3p\ {}^3P_g$ states of helium. Just as with helium the cross sections for excitation of the ${}^3P_g$ states exhibit their maxima when the electron is scattered at right angles to the direction of the incident beam. Due to the high probability of this process the anomalous $\sin^2\theta$ scattering pattern should be relatively easy to observe for beryllium. Furthermore, as in the case of helium the polarized radiation arising from subsequent dipole emission[24] should provide a useful diagnostic tool.

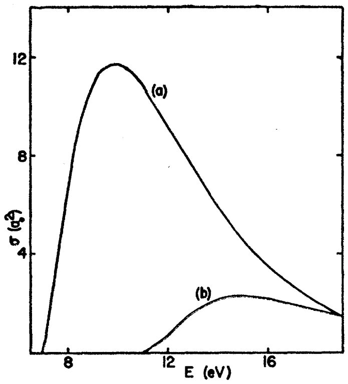

FIG. 6. Born-Oppenheimer cross sections for impact excitation of two states of beryllium. The total cross sections are given as functions of the incident electron energy. Curves (a) and (b) refer to the $(1s)^2(2p)^2$ and the $(1s)^2 2p3p\ {}^3P_g$ states, respectively.

The adequacy of the BO approximation to account for the double-excitation cross sections of beryllium must be verified by the performance of DEW and/or TS calculations of the sort which we have presented here for helium. It is possible that the BO cross sections may be in error by as much as an order of magnitude. However, even if this turns out to be the case one still could classify electron-impact production of doubly-excited beryllium as a rather efficient process. The BO calculations presented in this appendix constitute little more than an exploratory investigation. A more comprehensive study of the doubly-excited states of beryllium and of other alkaline earths is in progress and will be reported in a future communication.

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[24] I. C. Percival and M. J. Seaton, Phil. Trans. Roy. Soc. London **A251**, 113 (1958).